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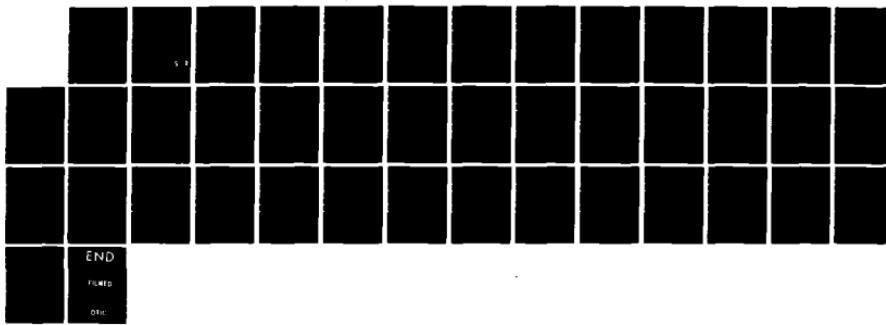
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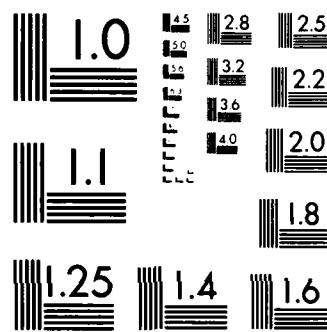
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The Electronic Spectra of Phthalocyanine Radical Anions and Cations

BY

P.C. Minor, M. Gouterman and A.B.P. Lever

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THE ELECTRONIC SPECTRA OF PHTHALOCYANINE RADICAL ANIONS AND CATIONS

By P.C.Minor^{1a}, M.Gouterman^{1b} and A.B.P.Lever^{1a}

Abstract:

The oxidation and reduction of metal phthalocyanines give rise to at least six oxidation states whose electronic spectra are rationalised in some depth in terms of SCF energies, Coulomb and exchange integrals. It is shown that a single set of parameters can reproduce the Q band energies moderately well. Further this same set of energies can reproduce differences in electrochemical potentials observed within this redox set. The pattern of variation in the Q band energies (and in their number) now provides a means for identifying whether it is the metal or the phthalocyanine ligand which is reduced upon addition of an electron to the system.

Introduction

During the past few years, there has been considerable resurgence in interest in the chemistry of the phthalocyanines (Pc). Their high thermal and chemical stability, coupled with their extensive redox chemistry makes them excellent candidates for electrocatalytic and

photocatalytic processes.²⁻⁵

The ultimate intention must be to possess sufficient understanding of the electronic structure of these molecules to be able to design catalysts to function in a specified fashion.

Recently our understanding of the electronic spectra of typical MPC complexes (containing the stable oxidation state $Pc(2-)$) has been extended to include charge transfer transitions.⁶ We have also presented a detailed explanation of the redox characteristics of these systems as a function of metal ion, oxidation state, solvent, substituent etc.⁷

Photo- or electroredox cycles involving main group MPcs will necessarily proceed via Pc anions or Pc cations. An analysis of the electronic spectra of such species should provide a clearer appreciation of how such systems might be involved in a catalytic process.

Initial Observations

The electronic structure of the $Pc(2-)M(n)$ species can be understood through the work of Gouterman and co-workers.⁸⁻¹⁰ Fig.1 illustrates the sequence and energies of the molecular orbitals lying near the HOMO and LUMO levels, which are of relevance to this spectroscopic study.

The two principal visible region features are the Q band ($1a_{1u}(\pi) \rightarrow 1e_g(\pi^*)$) near 600 - 750 nm with its associated vibrational satellites, and the B or Soret band ($1a_{2u}(\pi) \rightarrow 1e_g(\pi^*)$) near 325 - 425 nm. Several intense ultraviolet region transitions include $\pi-\pi^*$ transitions from deeper lying π -orbitals to $1e_g(\pi^*)$, e.g. the N band ($1b_{1u}(\pi)$, $2a_{2u}(\pi)$ or $1b_{2u}(\pi) \rightarrow 1e_g(\pi^*)$).^{10,11} There is some

evidence⁸⁻¹⁰ that shoulders on the lower energy edge of the Soret may be transitions of the $n\pi$ type from peripheral (bridging) azo links. These orbitals are located, energetically, near the HOMO level.^{10,11} Except for those indicated above, no Pc localised electronic spin allowed electronic transitions are expected energetically below the Soret. However where empty metal d orbitals lie inside the HOMO-LUMO gap, LMCT transitions of the general type $Pc(\pi) \rightarrow d$ may be anticipated. These can occur in the near ir, below the Q band, or between the Q and Soret absorption as has been extensively discussed.^{6,13}

$Pc(-2)M$ may be sequentially reduced up to four times by addition of electrons to the $leg(\pi^*)$ LUMO level. One or two electron oxidation occurs by removal of electrons from l_{1g} HOMO. Clack and Yandle¹² have prepared many of the anionic species by chemical reduction and have reported their electronic spectra. Lever and Myers¹⁴, and Hush and co-workers¹⁵ reported a collection of cation radical $Pc(-1M)(n)$ data. This work represents the first systematic assignment and detailed interpretation of this body of data. Each oxidized or reduced species has a characteristic spectrum which may include low energy absorption in the near infrared, multiple Q or Soret region absorption and additional charge transfer (CT) transitions.

Table 1 summarises the relative energies of a range of main group and transition metal phthalocyanine radical anions and cations. Well defined trends are clearly indicated in that most of the complexes behave in a parallel fashion. This is an important observation since it provides a means of identifying the various oxidised and reduced species. Since metal redox processes may reasonably be excluded on energetic grounds for main group

metals such as magnesium, and closed sub-shell species such as zinc, the reduction of such species in four steps must yield $Pc(-x)M(II)$, $x = 3,4,5$, and 6. Similarly, oxidation of the neutral species will yield $Pc(x-2)M(II)Y_x$ where $x = 1,2$ and Y is a counter-anion.

Indeed as illustrated graphically in Fig. 2, the Q band varies as follows. Beginning with the cation radical $Pc(-1)M$ (band usually near $18,000\text{ cm}^{-1}$), reduction to $Pc(-2)M$ results in a more intense red shifted Q band. Further reduction to $Pc(-3)M$ causes new absorption which is best interpreted in terms of the appearance of two new Q bands both blue shifted, and of lower intensity than $Pc(-2)M$. Subsequent reduction to $Pc(-4)M$ results in a spectrum with a single broad Q band which is yet further blue shifted. Reduction to $Pc(-5)M$ now results in a red shift in the Q band. Finally reduction to $Pc(-6)M$ causes the $leg(\pi^*)$ level to be filled such that no Q bands are possible. However, a pair of new absorption bands some 4000 cm^{-1} apart appear in the red end of the visible region and, as will be seen, are associated with the $leg(\pi^*)$ level. All of the main group complexes so far studied, and some of the transition group complexes behave in a manner exactly analogous to that described here. Such complexes are defined here as 'well behaved'.

With transition metal species such as $[Pc(-2)Fe(II)]$, redox can occur either at the metal or the ligand. From previous work¹⁶⁻¹⁸ it is known that the first reduction in both $Fe(II)Pc$ and $Co(II)Pc$ occurs at the metal to yield $[Pc(-2)M(I)]^-$. Where the data parallel the main group species, i.e. are well behaved, subsequent reduction can be assumed to occur at the ring and not the metal. Any deviations from regular behaviour should signal a change in oxidation state (or possibly spin state) at the metal. In general

esr and magnetic data can also indicate whether redox has occurred at the metal or ring. Thus, for example in the cobalt Pc system, reduction of $\text{Pc}(-2)\text{Co(II)}$ to $\text{Pc}(-2)\text{Co(I)}$ occurs, followed by behaviour paralleling that of zinc Pc described above, i.e. subsequent reduction occurs to the ring of the Co(I)Pc system.

The transition group phthalocyanines generally show some additional features which are likely to be charge transfer in origin.

Results and Discussion

As a starting point it is assumed that the one electron energies of the various π and π^* orbitals do not vary very much from one oxidation level to another. This is a reasonable assumption based on the fact that an 18 π -electron system is being considered and therefore loss or gain of one or two electrons has little effect upon bond order. Moreover the molecular geometry is fairly rigid. Note the similarity, for example, between the x-ray structural characteristics of ZnTPP and its radical cation ZnTPP^+ .¹⁹

Thus in a cation radical, changes in spectra will reflect the existence of a 'hole' in $1a_{1u}$ (and hence additional transitions e.g. of the type $e_g(\pi)-1a_{1u}(\pi)$ are expected), and changes in spin pairing energy. In addition a small change in geometry may be anticipated for anion radicals. Thus the mono-anion radical $\text{Pc}(-3)\text{M}$ will possess a 2E_g ground term which is subject to Jahn-Teller distortion. Although the degree of distortion cannot be very large because of the stereochemical rigidity of the molecule, it is sufficiently large to cause spin pairing in the di-anion radicals $\text{Pc}(-4)\text{M}$ which, for main group metals, are known to be diamagnetic^{12,20}, as

discussed below.

Our concern is to understand the regular shift in Q band indicated in Fig. 2, assign all the bands in the spectra of the various species (Table 1), derive some fundamental energy information from the spectroscopic changes, and indicate a relationship between spectroscopically and electrochemically defined energy parameters. In particular, our discussion represents a simplification of earlier work by Hush²¹ and by Linder et al.²² that we hope will be more useful for the experimentalist; also, we will discuss more explicitly the role of the Jahn-Teller effects in these systems.

Except where indicated below, the literature assignments of ring oxidation or reduction are accepted. On these bases, the spectroscopic data may be interpreted. First a qualitative discussion is presented for comparison with the experimental data and then, later, a semi-quantitative analysis attempted.

i) Cation radical $Pc(-1)M(n)$: The ground state configuration, $(a_{2u})^2 a_{1u}$, gives a $^2A_{1u}$ state. The following consequences may be predicted, relative to the unoxidized $Pc(-2)M$ species:

- a) The Q band shifts to high energy due to differential spin pairing energy, as discussed below.
- b) The Soret and N band should be little affected compared with the $Pc(-2)M$ species.
- c) The presence of a hole in a_{1u} permits allowed transitions from $e_g(\pi)$ levels lying below the a_{1u} .

Indeed, bands attributable to the Q, Soret, and N bands are readily identified in the spectra of the cation radicals, as shown in Table 1. From

its energy and intensity the band near 12,000 cm^{-1} is reasonably associated with $^2\text{E}_g \leftarrow ^2\text{A}_{1u}$ ($1\text{e}_g(\pi) \longrightarrow 1\text{a}_{1u}(\pi)$) as proposed. There is, however, an additional strong feature lying between the Q and Soret bands. This cannot arise via excitation from $\pi--\pi^*$ nor from a charge transfer transition or it would also be observed in the un-oxidised species. Thus it must be associated with the hole in 1a_{1u} . At lower energies there is a second orbital $2\text{e}_g(\pi)$ (Fig. 1), and transition therefrom to 1a_{1u} seems a proper assignment for this extra feature. Some care must be exercised in interpreting solid state spectra since broadening and extra peaks may arise through intermolecular coupling (Davydov splitting). However, the agreement between predicted and observed spectra is good and the assignments are probably correct.

ii) Mono-anion $\text{Pc}(-3)\text{M}(n)$: The ground electron configuration, $(\text{a}_{1u})^2\text{e}_g$ produces a degenerate term $^2\text{E}_g$. The following consequences are expected:

- a) Again, the Q band shifts to higher energy due to a difference in spin pairing energy, as discussed below.
- b) The ground state $^2\text{E}_g$, is subject to a JT distortion. However, this is not expected to be large enough to dominate the spectroscopic effects, since the JT effect of the configuration $(\text{a}_{1u})^2\text{e}_g$ of the mono-anion should be comparable to that of the Q band of the neutral, a_{1u}e_g . For the latter the small Stokes shift between absorption and fluorescence shows that the JT effect is small.
- c) The Q band arises from the configuration $\text{a}_{1u}(\text{e}_g)^2$, which gives rise to states $^4\text{A}_{2u}$, $^2\text{A}_{1u}$, $^2\text{A}_{2u}$, $^2\text{B}_{1u}$, $^2\text{B}_{2u}$. Electron exchange terms are expected to lift the degeneracy of the four doublet states, thus

explaining the presence of two bands in the Q region, $1200-2200 \text{ cm}^{-1}$ apart, as discussed below.

d) Allowed far red bands arise from the $\pi^*-\pi^*$ transitions

$1e_g(\pi^*) \longrightarrow 1b_{n_u}(\pi^*)$, ($n=1,2$) where $1b_{1u}(\pi^*)$ and $1b_{2u}(\pi^*)$ are higher energy π^* MO's of the neutral (Fig. 1). These $^2B_{1u}$ and $^2B_{2u}$ excited states have symmetries similar to two of the four 2Q states mentioned above.

e) There will be four Soret excited states with the same symmetries as the 2Q states. Thus two of the 2Q states will be subject to configuration interaction (CI) as in the neutral, and two will experience CI from states both to lower and higher energies; these latter may not then be moved by CI. The well-resolved far red band at $10,400 - 11,000 \text{ cm}^{-1}$ with which the spectrum begins, shows satellites 1000 and 2000 cm^{-1} to the blue, which are probably vibronic overtones.

iii) Di-anion $\text{Pc}(-4)\text{M}(n)$: As an open shell, the ground state $(a_{1u})^2(e_g)^2$ would be expected to be a triplet. However experimental studies²² show it is a singlet. As discussed below this can be explained by a pseudo JT effect that stabilizes $^1B_{1g}$ with respect to $^3A_{2g}$. The following spectroscopic effects may be expected.

a) The Q states, arising from the configuration $a_{1u}(e_g)^3$, have symmetry 2E_u , which are subject to a JT effect as in the neutral. This combined with the pseudo JT effect in the $^1B_{1g}$ ground state should lead to a broadened absorption, as is observed. A Soret band is expected and is observed at $30,000 \text{ cm}^{-1}$.

b) Additional transitions, $\pi^*-\pi^*$, as in the mono-anion are expected.

However, unlike the mono-anion, the absorption in the near infrared does not begin with a sharp band followed by a weaker vibronic. Rather it begins with a progression of two or three vibronics of comparable intensity¹². This difference from the mono-anion we ascribe to the pseudo-JT distorted ground state combined with the JT distorted excited configuration $(a_{1u})^2 e_g b_{1u}$.

iv) Tri-anion $Pc(-5)M(n)$: The ground configuration, $(a_{1u})^2 (e_g)^3$ gives rise to a 2E_g state, which should have a small JT distortion as in the mono-anion.

a) The Q band arising from the configuration $a_{1u}(e_g)^4$ and the Soret band arising from $a_{2u}(e_g)^4$ have excited states $^2A_{1u}$ and $^2A_{2u}$ respectively, which are not subject to mutual configuration interaction.

b) The $\pi^*-\pi^*$ excited states have configurations $(e_g)^2 b_{1u}$ or $(e_g)^2 b_{2u}$. These give rise to two transitions to the red of the Q bands in $Pc(-5)Mg(II)$ at 9,000 and 12,000 cm^{-1} . These states can have configuration interaction with the Q excited states, since they produce terms $^2A_{1u}$, $^2A_{2u}$, $^2B_{1u}$, $^2B_{2u}$.

v) Tetra-anion $Pc(-6)M(n)$: The e_g orbitals are now filled and the ground state is $^1A_{1g}$.

a) No Q or Soret bands are seen or are expected.

b) Excited states observed at $\sim 12,000$ and $\sim 16,000 \text{ cm}^{-1}$ can be attributed to $\pi^*-\pi^*$ transitions, $e_g(\pi^*) \longrightarrow b_{1u}(\pi^*), b_{2u}(\pi^*)$. These are significantly to the blue of the $\pi^*-\pi^*$ transition of the less reduced anions. Linder et al²², who did detailed calculations on the anions showed that use of neutral phthalocyanine orbitals can give a poor fit to the energies and that SCF orbitals of the tetra-anion must be used.

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We conclude that i) the high degree of regularity in the spectra of the many redox species from one metal to another, and the ability to fit the spectra with parameters whose values are most reasonable, must provide confidence in the veracity of the assignments, ii) species whose spectra are inconsistent must have anomalous redox behaviour, iii) following from these arguments, the electronic spectra of any Pc species in the redox range $\text{Pc}(-6)$ to $\text{Pc}(-1)$ can now reasonably be characterised by its electronic spectrum (supported where possible with associated esr data etc), and iv) as previously seen in the discussion of the CT energies in transition metal Pc species⁶, there is a good correlation between Pc electronic spectroscopy and electrochemical behaviour. The configurational mixing of the Q and Soret states is certainly smaller than in the porphyrins, where this mixing is considerable⁸⁻⁹. It is this purity in the Q state which probably contributes in a major fashion to the success of this simple treatment, to the success previously seen in correlating CT energies, and to the simple correlations which can be drawn between electronic spectroscopy and electrochemistry.

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We have previously noted⁶ in comparing phthalocyanine redox potentials and electronic charge transfer energies, that the inner reorganisation energy is small because there are so many electrons that exciting one has little effect upon molecular dimensions. The outer reorganisation energy is small because excitation of one of these many electrons, especially in this case, has little effect upon the solvation energy. Thus χ_1 and χ_0 in (11) can be ignored. In this case it is necessary if $E_{op} = nF\Delta E(\text{redox})$ that:

$$-Q = \Delta\Delta G_s + \Delta(\text{sol}) = \Delta G_s + \Delta G_s^* - \Delta G_s^+ - \Delta G_s^- \quad (12)$$

Within the terminology of Hush, we may write:

$$2\alpha = -(2\Delta G_s - \Delta G_s^+ - \Delta G_s^-) \quad (13)$$

but in the case of the phthalocyanines with such a large aromatic ring over which to delocalise the excited state charge, it is probably a good approximation to write $\Delta G_s^* = \Delta G_s$. Further the self-quenching energy may be written in terms of J and K integrals such that (12) becomes (14):

$$-(\Delta G_s + \Delta G_s^* - \Delta G_s^+ - \Delta G_s^-) = 2\alpha = -J_{ax} + 2K_{ax} \quad (14)$$

With this substitution an expression for $\Delta(-FE^0)$ can be written in terms of the various molecular J and K integrals, as shown in the sixth column of Table 3. Using the numerical values from (8), we obtain the calculated values in the sixth column of Table 3. The qualitative agreement between the experimental and calculated numbers (columns 5 and 6 of Table 3) is remarkably good.

In writing Eq. (14), molecular integrals are being related to solvation energy. At first thought this seems rather unlikely, as the one quantity is intra-molecular and the other is inter-molecular. However, although there has not been much systematic study, it appears that the Pc ring redox potentials E^0 have little solvent dependence and their differences even less. This is in spite of the term 2α appearing in $\Delta(-FE^0)$, Table 3 column 5.

of the couple. These are related to the reduction potentials, E° , following Hush²¹ by:

$$-FE^{\circ} - C = \Delta W + (n_f^2 - n_i^2)\alpha. \quad (10)$$

Here F is the Faraday; C is the constant which depends on the choice of reference electrode; n_i and n_f are the charges of initial and final species; and α is the free energy of solvation of the mono-anion and mono-cation, here considered an equal negative number. By taking differences in E° values the arbitrary constant C is eliminated. From ΔW and Eq. (10) we obtain expressions for the differences in (9), $\Delta(-FE^{\circ})$, which are given in the fifth column of Table 3 in terms of the parameters in (8).

It was noted some time ago that the difference in redox potentials for oxidation and reduction of the neutral porphyrin corresponds approximately to the lowest $\pi-\pi^*$ transition energy³².

Recently we³³ have explored the relationship involving the optical transition energy (E_{op}) between the orbitals ψ_g and ψ_e in a complex and the difference in oxidation potential for oxidation at ψ_g and reduction at ψ_e $\Delta E(\text{redox})$.^{33,34} This was written:

$$E_{op} = \chi_i + nF\Delta E(\text{redox}) + \Delta\Delta G_s + Q + \chi_o + \Delta(\text{sol}) \quad (11)$$

where χ_i and χ_o are the inner (vibrational) and outer (solvation) reorganisation energies, Q is the gas phase self-quenching energy (ground state molecule quenching of an excited state molecule to yield the reduced and oxidised species as the electron transfer products),

$\Delta\Delta G_s = 2\Delta G_s - \Delta G_s^+ - \Delta G_s^-$, $\Delta(\text{sol}) = \Delta G_s^* - \Delta G_s$, and ΔG_s , ΔG_s^* , ΔG_s^+ and ΔG_s^- are the solvation free energies of the neutral ground state, excited state, cation and anion respectively.

states, which red shifts the Q band. However, in the mono-cation and di-anion there is also CI between, respectively, the lower energy $\pi-\pi$ and the $\pi^*-\pi^*$ states and the Q state that cancel the red shift to some extent. In the tri-anion there is no CI between Q and Soret states so that there is less counter weight to CI with the lower energy $\pi^*-\pi^*$ states and the resultant blue shift. The net result is that the Q state in the neutral has an extra red shift with respect to the ionic species. The effect of CI in the mono-anion is complicated by the fact that only some of the four Q states have CI with the lower energy $\pi^*-\pi^*$ states (Table 4). Overall, the CI effects on the energy would seem to be small.

Finally can we correlate these results with electrochemical data? Consider that a well defined pattern emerges^{7,16,17} if one views the differences between reduction potentials of various species. Thus:

$$\begin{aligned} E(Pc(-1))-E(Pc(-2)) &= \text{ca. } 1.6-1.7 \text{ eV} = \text{ca. } 13,300 \text{ cm}^{-1} \\ E(Pc(-2))-E(Pc(-3)) &= \text{ca. } 0.4 \text{ eV} = \text{ca. } 3,200 \text{ cm}^{-1} \\ E(Pc(-3))-E(Pc(-4)) &= \text{ca. } 0.6 \text{ eV} = \text{ca. } 4,800 \text{ cm}^{-1} \\ E(Pc(-5))-E(Pc(-6)) &= \text{ca. } 0.4 \text{ eV} = \text{ca. } 3,200 \text{ cm}^{-1} \end{aligned} \quad (9)$$

It should be possible to calculate these differences in energy in terms of the optical parameters described above, by re-grouping them in terms of the energy parameters used in the optical spectroscopy discussion. Thus the energy, ΔW necessary to add an electron, in the gas phase, to the cation $Pc(-1)$ is ϵ_a , while the energy, ΔW , necessary to reduce the neutral to the mono-anion $Pc(-3)$, also in the gas phase is ϵ_x . Values for these and the other species are shown in column 3 of Table 3. In solution it is necessary to take into account the difference in solvation energy of the two partners

ground state of the di-anion. Moreover we assume $K_{ax} = K_{xy}$. By analysis of the expressions for the Q band transition energies, it is possible to group the variables into four parameters as shown in Table 2, namely:-

$$\Delta E = \epsilon_x - \epsilon_a - J_{ax}; J_{aa} - J_{ax}; J_{xx} - J_{ax}; K_{xy}. \quad (7)$$

These have been fitted to the average Q band energies displayed by the $Pc(-1)$, $Pc(-2)$ and $Pc(-3)$ species. As shown in Table 2, the best fit is obtained with:-

$$\Delta E = 12,300; J_{aa} - J_{ax} = 5400; J_{xx} - J_{ax} = 3200; K_{xy} = 1100\text{cm}^{-1} \quad (8)$$

which reproduce the behaviour of these three oxidation states moderately well. The absorption energies of the $Pc(-4)$ and $Pc(-5)$ species, as well as the triplet transition of the $Pc(-2)$ species³¹ have also been calculated. Although the fit to these latter species is not so favourable, they are qualitatively correct in showing that the di-anion and tri-anion, like the cation, are blue shifted with respect to the neutral species (Table 2).

What factors enter a more exact treatment? We have conceptually extended the SCF energies from the neutral to the other species. Linder et al.²² showed that calculations on the tetra-anion $\pi^* - \pi^*$ transitions totally failed when orbitals of the neutral were used, and for a good fit it was necessary to use the SCF orbitals of the tetra-anion itself. It is reasonable to expect that in the higher anions the energy gap between $a_{1u}(\pi)$ and $e_g(\pi^*)$ might decrease [i.e., ΔE decreases], thus explaining why our calculated energies for $Pc(-4)$ and $Pc(-5)$ are too large. A second factor that enters is configuration interaction (CI) between the Q state and other excited states. The various state symmetries are listed in Table 4. In all cases except the tri-anion there is CI between the Q and the Soret

the di-anion 1E_u excited state, and the tri-anion 2E_g ground state. This is illustrated schematically in Fig. 3. The largest JT effect would naively be expected for configurations $[e_g(\pi^*)]^2$, which occur in the mono-anion excited state and the di-anion ground state. Here the states $(e_{gx})^2$ have twice the JT stabilization as $(e_{gx})^1$ or $(e_{gx})^2e_{gy}$; the states $e_{gx}e_{gy}$ would have no JT effect. However, the states $(e_{gx})^2$ and $(e_{gy})^2$ are subject to configuration interaction and the JT effect becomes second order or a "pseudo Jahn-Teller" effect ³⁰. This result is again illustrated in Figure 3 for the mono-anion excited state $^2B_{1u}$, and the di-anion ground state, $^1B_{1g}$. The doubling of the mono-anion Q band is attributed to the exchange energy splitting of the four doublet states that arise from the configuration $a_{1u}(e_g)^2$; the Jahn-Teller effect contributes some vibronic broadening. For the di-anion ground state the pseudo JT effect is very important, as it may be partly responsible for the fact that the ground state is $^1B_{1g}$ rather than $^3A_{2g}$, as shown in Figure 3D. We attribute the great broadness observed in the di-anion Q bands to the combination of the pseudo JT effect in the ground state and the JT effect in the excited state.

It would be useful to calculate the transition energies for the observed Q bands to rationalise the experimental data and also to relate these to the electrochemical data. Expressions for the Q band excited state energies are shown in Table 2 in terms of the SCF energies of a_{1u} and e_g defined as ϵ_a and ϵ_x respectively, and the necessary Coulomb and exchange integrals, specifically J_{aa} , J_{xx} , J_{xy} , K_{ax} and K_{xy} , a total of seven variables in all. We follow Hush²¹ and assume $J_{xx} = J_{xy}$ to account for the singlet

however it is extremely difficult to obtain accurate intensity data for the reduced species; thus the literature values probably contain significant experimental error. Moreover the simple molecular orbital analysis²⁸ used to obtain the relative oscillator strengths is not expected to be highly accurate.

Several features can be seen in Table 2 and 3. Note that for the cation and the neutral, the transition is from a simple non-degenerate ground state to a degenerate excited state. This degeneracy implies a Jahn-Teller effect. The mode of operation of the JT effect is shown in Fig. 3. For $Pc(-1)$ and $Pc(-2)$ the effect is simply to shift the minimum of the excited state with respect to the ground state. The result would be to introduce a Franck-Condon progression in the Jahn-Teller mode.²⁹ The excited state and ground state potentials would then be described by the oscillator equations

$$H = \hbar\omega[(p^2 + q^2) + \lambda q] \quad (4)$$

where $\lambda=0$ in the ground state but $\lambda\neq0$ in the excited state. The JT energy defined in Fig. 3A is just $(\lambda^2/2)\hbar\omega$. It can be shown³⁰ that the ratio

$$I(n,0)/I(0,0) = (\lambda^2/2)^n/n! \quad (5)$$

where $I(n,0)$ is the intensity of the transition to the n th level in the JT mode and $I(0,0)$ is the intensity of the origin. In particular

$$\begin{aligned} I(1,0)/I(0,0) &= \lambda^2/2 = (\text{JT energy})/(\text{vibrational quantum}) \\ &= <0.2. \end{aligned} \quad (6)$$

The estimate 0.2 comes from standard spectra for $Pc(-2)$.

The JT effect arises because of one extra electron in an $e_{gx}(\pi^*)$ orbital, and is expected to be comparable for the mono-cation 2E_g excited state, the neutral 1E_u excited state, the mono-anion 2E_g ground state,

We shall start with the one electron Hartree-Fock operator for the neutral ground state.

$$F = H^{\text{core}} + \sum_j (2J_j - K_j) \quad (1)$$

Here H^{core} is the one electron operator for electron kinetic energy and its Coulomb potential energy interaction with the nuclei and any electrons in a frozen core; the J_j and K_j are Coulomb and exchange operators that depend on the doubly occupied orbital ϕ_j of the neutral ground state as defined by Roothaan²⁷. For molecular orbitals we have

$$F\phi_k = \epsilon_k \phi_k \quad (2)$$

where ϕ_k are the SCF orbitals and ϵ_k are the SCF energies of the neutral ground state. For any orbital ϕ_i we have:

$$\langle \phi_i | J_j | \phi_i \rangle = J_{ij}; \langle \phi_i | K_j | \phi_i \rangle = K_{ij} \quad (3)$$

Here J_{ij} and K_{ij} are Coulomb and exchange integrals with their usual definition²⁸. In Table 2 we list the energies for transitions from the ground to the Q state, i.e. the transition $1a_{1u}(\pi) \rightarrow 1e_g(\pi^*)$, in terms of ϵ_i and the various J_{ij} and K_{ij} . In doing this the orbital energies are assumed to remain invariant as in the neutral and we calculate the energies at the D_{4h} equilibrium position. In Table 3 we have listed the energy for reduction of each species in this same approximation. Tables 2 and 3 then represent a simple treatment of factors (1) and (2), the orbital energy differences and the differences among Coulomb and exchange integrals.

Table 2 also contains an estimate of the relative oscillator strengths of the various redox species normalised to the oscillator strength of the neutral (-2) species. In fact agreement with experiment is rather poor -

parallel the data for the main group analogs, but with one additional charge transfer band (LMCT). It is likely therefore, that they are $\text{Pc}(-4)\text{Mn(II)}$ and $\text{Pc}(-5)\text{Mn(II)}$, i.e. reduction occurs at the ring. Esr data support this conclusion^{25,26}, though with some ambiguity concerning $\text{Pc}(-4)\text{Mn(II)}$. The species $\text{Pc}(-6)\text{Mn(II)}$ has the usual doublet $\pi^*-\pi^*$ transitions but the CT band is curiously absent. Possibly it has shifted to very low energy (out of range of this study) since the Pc unit is now very readily oxidisable.

The spectra for the nickel(II) Pc species exactly parallel the main group data since no change in oxidation state of the nickel ion is expected¹⁸ and no charge transfer is expected in the region under study.⁶

In summary, the main group complexes, nickel and cobalt species all have parallel 'well behaved' deportment. The lower oxidation states of the manganese species are also well behaved but there are evidently some subtle changes in redox behaviour for the iron series.

ii) Semi-quantitative approach: There are four factors that need to be considered in discussion of the spectra of the anions. Listed in what we consider their order of importance, these are: (1) the one electron energy difference between the orbitals of the transitions; (2) the two electron Coulomb and exchange integrals, i.e. the change in repulsion energy due to the transition; (3) the Jahn-Teller and pseudo Jahn-Teller effects; and (4) configuration interaction among the various states.

Linder et al²² did a quite careful treatment of ground and excited states of the mono-, tri-, and tetra-anions. Our goal is to present a simpler treatment that we hope will be more accessible to the experimentalist yet still useful for understanding the observed spectroscopic generalities.

this transition.

In the case of the species $[\text{Co(I)Pc(-4)}]^{3-}$, the Q and CT bands overlap to yield a very strong feature near $20,000 \text{ cm}^{-1}$.

The species $[\text{Pc(-1)Fe(III)}]^{2+}$, $[\text{Pc(-2)Fe(III)}]^+$, $[\text{Pc(-2)Fe(II)}]$ and $[\text{Pc(-2)Fe(I)}]^-$ have spectra as anticipated. The species $[\text{Pc(-2)Fe(I)}]^-$ ^{16,17} has an extra strong band near $20,000 \text{ cm}^{-1}$ reasonably assigned as charge transfer from Fe(I) to P_c(-2) (probably $d(xz, yz) \cdots 1b_{1u}(\pi^*)$) (MLCT), but the Q band appears unusually weak. However it is rather broad and the total integrated intensity may not have diminished a great deal. Indeed the peak molar intensity of the Q band does depend upon the oxidation state of the central metal ion, increasing, and becoming narrower with increasing oxidation state.¹³ The species formally at oxidation level P_c(-3)Fe(I) does not exhibit a doubling of the Q band but does show a strong additional band near $20,000 \text{ cm}^{-1}$ suggesting it is an Fe(I) species. This is in agreement with earlier studies. The species formally P_c(-4)Fe(I) does possess a normal spectrum but the charge transfer band is now missing. The P_c(-5)Fe(I) species is again atypical. Clearly the system requires further study for proper understanding, and this is in hand.²³

The first reduced manganese species is known²⁴ to be $[\text{Pc(-3)Mn(II)}]^-$ whose spectrum is very rich. While the doubled Q band may be identifiable, there are a significant number of additional strong features which are presumably charge transfer in origin⁶. Tripmultiplet transitions, though expected to be fairly weak, may well contribute to the complexity of the spectrum. A clear assignment of this species is not yet possible.

However the double and triply reduced species have spectra which

It is clear that the overall features of all the spectra agree in general with expectation. However, certain questions are immediately apparent. What are the assignments of additional bands seen in some of the transition metal phthalocyanine species? Are the absolute energies observed consistent with changes in spin pairing energy, Jahn-Teller splitting, changes in configurational interaction etc., and can any of these quantities be derived? Are there relationships between the electrochemical potentials for oxidation and reduction, and the observed transition energies?

i) Transition metal phthalocyanine CT spectra: Consider first the series of cobalt complexes $[\text{Pc}(-1)\text{Co(III)}]^{2+}$, $[\text{Pc}(-2)\text{Co(III)}]^+$, $[\text{Pc}(-2)\text{Co(II)}]$, $[\text{Pc}(-2)\text{Co(I)}]^-$, $[\text{Pc}(-3)\text{Co(I)}]^{2-}$... $[\text{Pc}(-6)\text{Co(I)}]^{5-}$ (where any axial ligands are omitted for clarity). This series behaves very much like a main group phthalocyanine once reduction to the $\text{Pc}(-2)\text{Co(I)}$ level is achieved, leading to the conclusion that the cobalt remains in the Co(I) state as reduction occurs at the ring.

An additional intense absorption occurs at $20,000 - 25,000 \text{ cm}^{-1}$ in all the reduced species containing Co(I) . A previous MCD study¹³ of $[\text{Pc}(-2)\text{Co(I)}]$ assigned this to a Co(I) to Pc MLCT transition. Since an A term was observed in the MCD spectrum, the excited state must be doubly degenerate; the probable assignment is $d(xz,yz) \longrightarrow \text{h}_{\text{blu}}\pi^*$. Using the electrochemical procedure for identifying charge transfer energies⁶, this transition is indeed predicted to lie in the region where this band is observed. The lack of any significant variation in the energy of this transition as the phthalocyanine is further reduced, does imply that the leg (π^*) level to which electrons are being added, is not involved, at least in first order, in

Table 1 The Electronic Spectra of Phthalocyanine Anions and Cations

	Co(III)Pc(-1)	Co(III)Pc(-2)	Co(II)Pc(-2)	Co(I)Pc(-2)	
$\pi-\pi(1)$	13,370				
Q	18,000	14,660	14,885	14,410(0.23)	
$\pi-\pi(2)$	22,570				
CT		28,650		21,410(0.76)	
Soret	28,550	27,170	28,735	32,050(vs)	
N	35,640				
Ref.	14	35	36	12	
	Cr(III)Pc(-1)	Cr(III)Pc(-2)	Zn(II)Pc(-1)	Si(IV)Pc(-1)	
$\pi-\pi(1)$	12,540		13,460	11,810	
Q	17,350	14,795	18,150	18,190	
$\pi-\pi(2)$	22,470		22,430	25,060	
CT					
Soret	27,590	29,070	26,360	34,920	
N	35,700	37,300	30,980?	39,980	
Ref.	14	36	14	15	
	Fe(III)Pc(-1)	Fe(III)Pc(-2)	Fe(II)Pc(-2)	Fe(I)Pc(-2)	
$\pi-\pi(1)$	12,220				
Q	16,740	14,970	15,250	19,420(0.24)	
$\pi-\pi(2)$	22,960				
CT		27,050		(a)	
Soret	27,030	28,410	30,350	30,670(0.75)	
N	36,360				
Ref.	14	35	36	12,17	
	Mg(II)Pc(-2)	Ni(II)Pc(-2)	ClAlPc(-2)	Mn(II)Pc(-2)	Zn(II)Pc(-2)
Q	14,900	14,900	14,500	14,700	14,685
Soret	29,410	28,490	28,570		28,820
Ref.	36	36	36	36	36

Table 1 cont

	MgPc(-3)	MgPc(-4)	MgPc(-5)	MgPc(-6)
$\pi^*-\pi^*(1)$	10,420(0.01)	--	8970(0.02)	11,910(0.21)
-V	11,630	11,110		
-V	12,530	12,500		
		16,260		
$\pi^*-\pi^*(2)$			12,120(0.08)	16,130(0.40)
Q	15,670(0.16)	19,230(0.62)	16,950(0.52)	
Q	17,790(0.24)	--	--	
Soret	23,810(0.20)	29,850(0.69)	29,500(0.88)	
Soret	29,410(0.085)			
UV				24,270(0.26)
UV				32,790(0.58)
Ref.	12	12	12	12

	ClAlPc(-3)	ClAlPc(-4)	ClAlPc(-5)	ClAlPc(-6)
$\pi^*-\pi^*(1)$	10,260(0.03)		9620(0.03)	12,350(0.09)
-V	11,110	11,110		
-V	12,200	12,500		
	13,810			
$\pi^*-\pi^*(2)$			13,330	16,560(0.16)
Q	16,180(0.07)	19,310(0.27)	17,040(0.20)	
Q	17,390(0.12)			
Soret	30,400(0.54)	30,580(0.49)	30,120(0.42)	
Soret	-	-		
UV				28,990(0.39)
Ref.	12	12	12	12

	ZnPc(-3)	ZnPc(-4)	ZnPc(-5)	ZnPc(-6)
$\pi^*-\pi^*(1)$	10,550(0.07)		9090(0.15)	12,180(vs)
-V	11,770	12,950		
-V	12,740			
$\pi^*-\pi^*(2)$				16,130(vs)
Q	15,720(s)	19,160(vs)	17,540(vs)	
Q	17,790(s)	--	--	
Soret	30,960(vs)	29,850(vs)	29,410(vs)	
Soret				
UV				32,890(vs)
Ref.	12	12	12	12

	NiPc(-3)	NiPc(-4)	NiPc(-5)	NiPc(-6)
$\pi^*-\pi^*(1)$	10,930(0.02)	10,990	9220(0.13)	11,360(0.93)
-V	11,830	11,360	11,240	
-V	12,350	11,770		
$\pi^*-\pi^*(2)$			14,880(s)	
Q	15,870(0.45)	18,660(s)	16,950(vs)	
Q	17,610(0.72)			
Soret	30,030(vs)	30,030(vs)	30,000(vs)	
Soret				
UV			32,150(vs)	
Ref.	12	12	12	12
	Co(I)Pc(-3)	Co(I)Pc(-4)	Co(I)Pc(-5)	Co(I)Pc(-6)
$\pi^*-\pi^*(1)$	10,870(0.05)	8480(0.06)	10,000	11,300(0.06)
-V		11,050(0.08)	11,490(0.1)	
-V				
$\pi^*-\pi^*(2)$			14,490(0.4)	
Q	14,680(0.18)	19,610(vs)	17,480(1.06)	
Q	16,000(0.14)			
CT	21,010(s)	(a)	23,700(0.52)	18,520(0.94)
Soret	31,350(vs)	30,670(s)	?	
Ref.	12	12	12	12
	MnPc(-3)	MnPc(-4)	MnPc(-5)	MnPc(-6)
$\pi^*-\pi^*(1)$			12,020(vs)	
-V				
-V	Very			
$\pi^*-\pi^*(2)$			16,130(vs)	
CT	Rich	14,120(0.43)	9090(0.5)	
Q	Complex	19,160(vs)	17,670(vs)	
Q				
Soret	Spectrum	30,210(s)	29,410(s)	
Soret				
UV			27,030(s)	
Ref.	12	12	12	12

Numbers in parentheses are oscillator strengths and s = strong, vs = very strong. For data for reduced iron species, see ref. [12]. a) Probably contained within Q band.

Table 2

 Transition Energies and Transition Moments for Q States of
 Phthalocyanine Species

Species	Transition	Energy ^{ab}	Transition Moment ^c
Pc(-1)	$2E_g \rightarrow 2A_{1u}$	$\Delta E + J_{aa} - J_{ax} + K_{ax} = 18.8^d$	R^2
Pc(-2)	$3E_u \rightarrow 1A_{1g}$	$\Delta E = 12.3^f (9.1-10.6^e)$	0
	$1E_u \rightarrow 1A_{1g}$	$\Delta E + 2K_{ax} = 14.5^d$	$4R^2$
Pc(-3)	$2B_{1u} \rightarrow 2E_g$	$\Delta E + J_{xx} - J_{ax} + K_{ax} - K_{xy} = 15.5^d$	$R^2/2$
	$2B_{2u} \rightarrow 2E_g$	$\Delta E + J_{xy} - J_{ax} + K_{ax} + K_{xy} = 17.7^d$	$R^2/2$
	$2A_{2u} \rightarrow 2E_g$	$\Delta E + J_{xy} - J_{ax} + 3K_{ax} - K_{xy} = 15.5^d$	$3R^2/2$
	$2A_{1u} \rightarrow 2E_g$	$\Delta E + J_{xx} - J_{ax} + K_{ax} + K_{xy} = 17.7^d$	$R^2/2$
Pc(-4)	$1E_u \rightarrow 1B_{1g}$	$\Delta E + J_{xy} + J_{yy} - 2J_{ax} + 3K_{ax}$ $= 22.0^f (19.0)^g$	$2R^2$
Pc(-5)	$2A_{1u} \rightarrow 2E_g$	$\Delta E + 2J_{xy} + J_{xx} - 3J_{ax} + 2K_{ax} - K_{xy}$ $= 23.0^f (17.3)^g$	R^2

a) Abbreviations:- $a = a_{1u}$, $x = e_{gx}(\pi^*)$, $y = e_{gy}(\pi^*)$. D_{4h} symmetry is assumed thereby fixing $\epsilon_x = \epsilon_y$, $J_{xx} = J_{yy}$, $J_{ax} = J_{ay}$, $K_{ax} = K_{ay}$.

b) $\Delta E = \epsilon_x - \epsilon_a - J_{ax}$. c) $R = \langle a_{1u}(\pi) | x | e_{gy} \rangle$. d) These numbers are rough averages of the data for these transitions for the main group phthalocyanines, and are fitted assuming $J_{xx} = J_{xy}$, $K_{ax} = K_{ay}$ and $\Delta E = 12,300$, $J_{aa} - J_{ax} = 5400$, $J_{xx} - J_{ax} = 3200$ and $K_{xy} = 1100 \text{ cm}^{-1}$.

e) Experimental data.³¹ f) Calculated using the values in (d).

g) Experimental numbers from Fig.2.

Table 3

Optical and Electrochemical Energies for Reduction of Phthalocyanine Species

Reduction Step	States	ΔW	$-FE^O - C$	$(-FE^O)^b$	$(-FE^O)^c$
Pc(-1) - Pc(-2)	$2A_u^- - 1A_{1g}$	ϵ_a	$\Delta W - \alpha$	$\epsilon_x - \epsilon_a + 2\alpha = 13,300$	$\epsilon_e - \epsilon_a - J_{ax} + 2K_{ax} = 14,500$
Pc(-2) - Pc(-3)	$1A_{1g}^- - 2E_g$	ϵ_x	$\Delta W + \alpha$		
Pc(-3) - Pc(-4)	$2E_g^- - 3A_{2g}$	$\epsilon_x + J_{xy} - K_{xy}$		$J_{xx} - K_{xy} + 2\alpha = 3200$	$J_{xx} - K_{xy} - J_{ax} + 2K_{ax} = 4300$
	$2E_g^- - 1B_{1g}$	$\epsilon_x + J_{xx} - K_{xy}$			
	$2E_g^- - 1B_{2g}$	$\epsilon_x + J_{xy} + K_{xy}$			
	$2E_g^- - 1A_{1g}$	$\epsilon_x + J_{xx} + K_{xy}$			
Pc(-4) - Pc(-5)	$1B_{1g}^- - 2E_g$	$\epsilon_x + 2J_{xy}$	$\Delta W + 5\alpha$	$2J_{xy} - J_{xx} + K_{xy} + 2\alpha = 4800$	$2J_{xy} - J_{xx} + K_{xy} - J_{ax} + 2K_{ax} = 6500$
				$J_{xx} - K_{xy} + 2\alpha = 3200$	$J_{xx} - K_{xy} - J_{ax} + 2K_{ax} = 4300$
Pc(-5) - Pc(-6)	$2E_g^- - 1A_{1g}$	$\epsilon_x + 2J_{xy} + J_{xx}$	$\Delta W + 7\alpha$		
				K_{xy}	

a) C depends upon reference electrode but cancels from the analysis. We assume with Hush²¹ that the free energy for ion solvation is $n^2\alpha$, where n is the species charge and α is a negative multiplier. b) This column is the difference between the entries in column 4 above and below it. The numbers (wavenumbers) are experimental averages from electrochemical data.⁷ c) The expressions in this column arise from column 5 replacing 2 by $-J_{ax} + 2K_{ax}$. The numbers are the solutions for these expressions using the optical data analysis in the text and the parameter values in Table 2.

Table 4
STATE SYMMETRIES IN PHTHALOCYANINE SPECIES

State	Pc(-1)	Pc(-2)	Pc(-3)	Pc(-4)	Pc(-5)	Pc(-6)
Ground	$^2A_{1u}$	$^1A_{1g}$	2E_g	$^1B_{1g}$	2E_g	$^1A_{1g}$
Q level	2E_g	1E_u	$^2A_{1u}, ^2A_{2u}$ $^2B_{1u}, ^2B_{2u}$	1E_u	$^2A_{1u}$	---
Soret	2E_g	1E_u	$^2A_{1u}, ^2A_{2u}$ $^2B_{1u}, ^2B_{2u}$	1E_u	$^2A_{2u}$	---
$\pi^*-\pi^*$	---	---	$^2B_{1u}, ^2B_{2u}$	1E_u	$^2A_{1u}, ^2A_{2u}$ $^2B_{1u}, ^2B_{2u}$	1E_u
$\pi-\pi$	2E_g	---	---	---	---	---

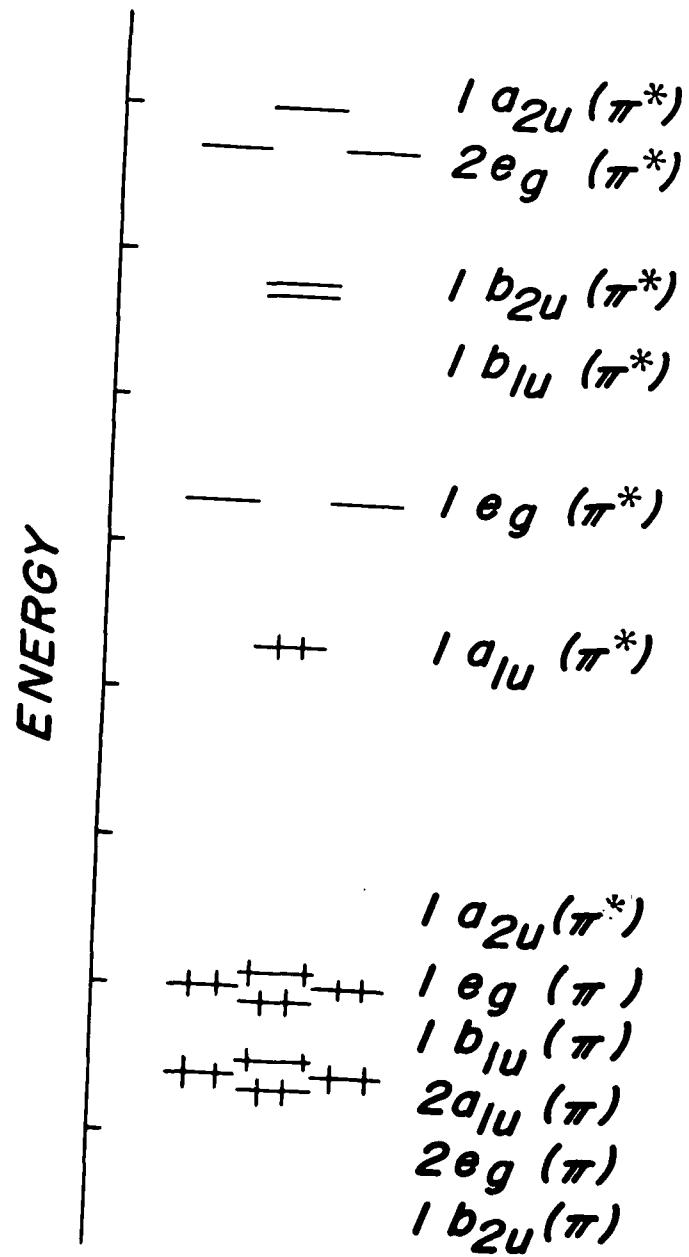
Q and Soret bands as usually defined. $\pi^*-\pi^*$ is transition from $1e_g(\pi^*)$ into $1b_{1u}(\pi^*)$ or $1b_{2u}(\pi^*)$. $\pi-\pi$ is transition from $1e_g(\pi)$ to $1a_{1u}$.

Figure Legends

Fig.1. Energies of the highest occupied and lowest unoccupied molecular orbitals⁸. The molecular orbitals are numbered sequentially, up and down, from the Fermi level.

Fig.2. Peak energies for the Q bands [$1a_{1u}(\pi)$ --- $1e_g(\pi^*)$] for $[Pc(-x)Zn]^{2-x+}$, $x = 1$ to 5.

Fig.3. Potential energy curves showing schematically the effect of a Jahn-Teller mode on the excited states of phthalocyanine species: A - mono-cation, B - neutral, C - mono-anion, D - di-anion, E - tri-anion. The arrow, in panel A, shows the definition of the JT energy.



F1g1 Level

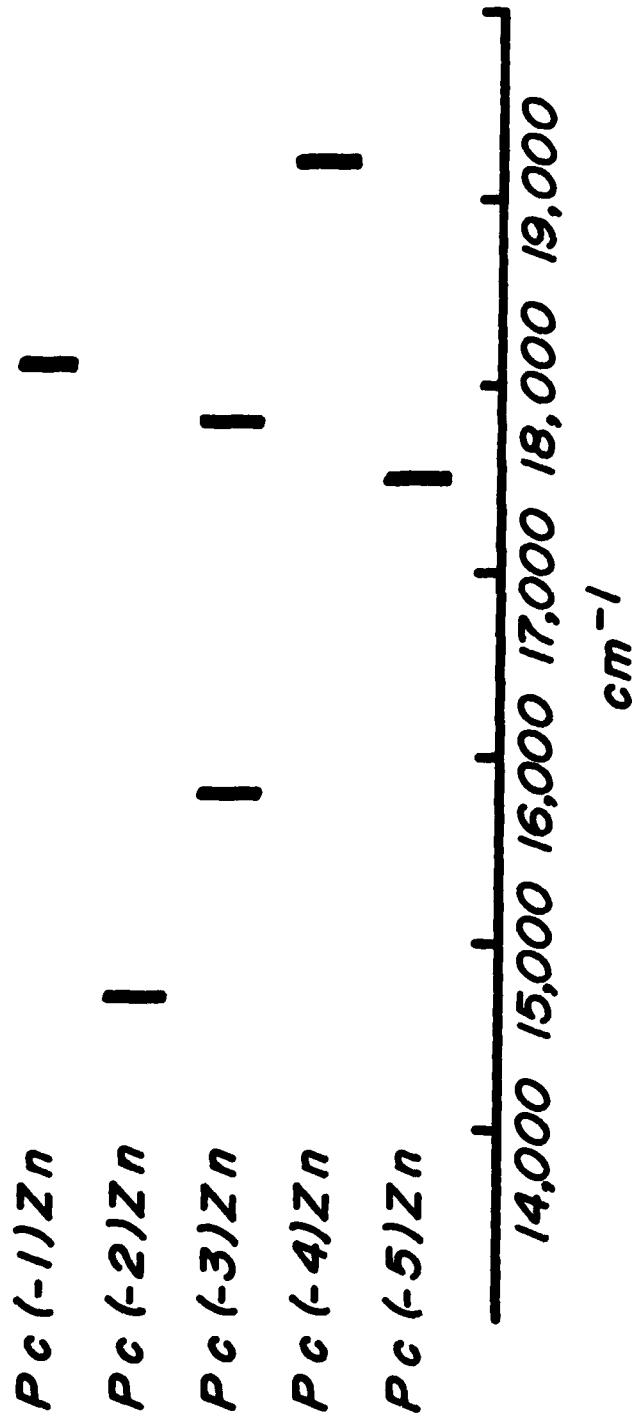


Fig. 2

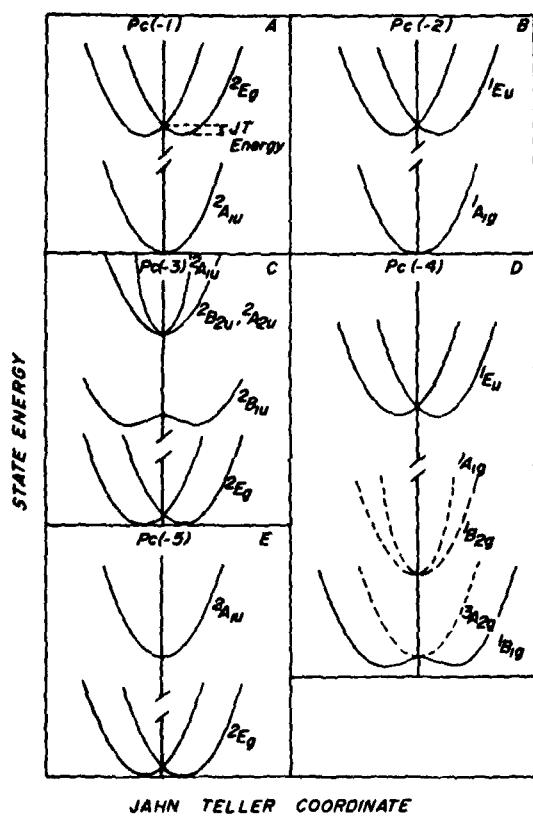


Fig 3

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Department of Chemistry
Oakland University
Rochester, Michigan 48063

Dr. H. Richtol
Chemistry Department
Rensselaer Polytechnic Institute
Troy, New York 12181

Dr. R. A. Marcus
Department of Chemistry
California Institute of Technology
Pasadena, California 91125

Dr. E. Yeager
Department of Chemistry
Case Western Reserve University
Cleveland, Ohio 44106

Dr. C. E. Mueller
The Electrochemistry Branch
Naval Surface Weapons Center
White Oak Laboratory
Silver Spring, Maryland 20910

Dr. Sam Perone
Chemistry & Materials
Science Department
Lawrence Livermore National Laboratory
Livermore, California 94550

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Department of Chemistry
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Salt Lake City, Utah 84112

Donald E. Mains
Naval Weapons Support Center
Electrochemical Power Sources Division
Crane, Indiana 47522

S. Ruby
DOE (STOR)
M.S. 6B025 Forrestal Bldg.
Washington, D.C. 20595

Dr. A. J. Bard
Department of Chemistry
University of Texas
Austin, Texas 78712

Dr. Janet Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Donald W. Ernst
Naval Surface Weapons Center
Code R-33
White Oak Laboratory
Silver Spring, Maryland 20910

Mr. James R. Moden
Naval Underwater Systems Center
Code 3632
Newport, Rhode Island 02840

Dr. Bernard Spielvogel
U.S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709

Dr. Aaron Fletcher
Naval Weapons Center
Code 3852
China Lake, California 93555

Dr. M. M. Nicholson
Electronics Research Center
Rockwell International
3370 Miraloma Avenue
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Dr. Michael J. Weaver
Department of Chemistry
Purdue University
West Lafayette, Indiana 47907

Dr. R. David Rauh
EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

Dr. Aaron Wold
Department of Chemistry
Brown University
Providence, Rhode Island 02192

Dr. Martin Fleischmann
Department of Chemistry
University of Southampton
Southampton SO9 5NH ENGLAND

Dr. R. A. Osteryoung
Department of Chemistry
State University of New York
Buffalo, New York 14214

Dr. Denton Elliott
Air Force Office of Scientific
Research
Bolling AFB
Washington, D.C. 20332

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Naval Research Laboratory
Code 6170
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Naval Ocean Systems Center
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Dr. Gregory Farrington
Department of Materials Science
and Engineering
University of Pennsylvania
Philadelphia, Pennsylvania 19104

M. L. Robertson
Manager, Electrochemical
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Naval Weapons Support Center
Crane, Indiana 47522

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Department of Chemistry
Northwestern University
Evanston, Illinois 60201

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Dr. Joseph Gordon, II
IBM Corporation
K33/281
5600 Cottle Road
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Dr. Hector D. Abruna
Department of Chemistry
Cornell University
Ithaca, New York 14853

Dr. D. H. Whitmore
Department of Materials Science
Northwestern University
Evanston, Illinois 60201

Dr. Alan Bewick
Department of Chemistry
The University of Southampton
Southampton, SO9 5NH ENGLAND

Dr. E. Anderson
NAVSEA-56Z33 NC #4
2541 Jefferson Davis Highway
Arlington, Virginia 20362

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University of California
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